

# SCIENCE FOR GLASS PRODUCTION

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## SURFACE ATTRACTIVE FORCES OF GLASS BATCH PARTICLES

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The forces of surface interaction between glass batch components are considered. A comparison between capillary and gravitational forces for particles of different sizes at different stages of glass batch preparation is carried out. The dependences of capillary force on the volume of liquid and the distance between particles are discussed.

The adhesion-capillary attractive force of glass batch grains fix the grain distribution after mixing and thus improve the homogeneity of the glass melt. When the batch is moistened, capillary water menisci fix chalk, lime, sulfate, and other component particles next to quartz sand grains. After the evaporation of drop water with increasing temperature there is capillary interaction of menisci consisting of salt and oxide eutectic melts. The particle conglomeration processes in glass batches have been considered in [1–4].

Theoretical and experimental analysis of the interaction between ideally smooth dry solid bodies (Fig. 1a) shows [5] that the force of their molecular attraction in direct contact is equal to  $2\sigma\pi R$  and  $4\sigma\pi R$  for sphere–sphere and plane–sphere contacts, respectively ( $R$  is the radius of a spheroid particle;  $\sigma$  is the surface tension of the material of the solid particles). However, as the solid bodies are brought apart, their molecular attraction force sharply decreases and at a distance of  $0.3–0.4\text{ }\mu\text{m}$  is equal to zero. Considering that solid particles due to their rough unpolished surfaces contact at the sites of microbulges of size  $1\text{ }\mu\text{m}$  or more, dry batch grains in fact are not attracted to each other.

Attractive forces of solid bodies that are close to the above specified values are observed in capillary adhesion, both in a zero clearance (Fig. 1b) and at a distance up to  $0.1\text{ mm}$  and more (Fig. 1c). The capillary strength of adhesion of particles via concave liquid menisci (Fig. 1b and c) depends mainly on the Laplace pressure differential. A mobile liquid-air interface deflects toward the phase whose pressure is lower.

In the general case the capillary interaction force  $f_{\text{cap}}$  generated by drop liquid is made up by the Laplace pressure

$\Delta P$  transmitted by the liquid via the section of the area  $\omega = \pi a^2$  ( $a$  is the radius of the wetting perimeter of a spheroid particle) and the force of the surface tension of liquid applied to the perimeter  $L = 2\pi a$ :

$$\Delta P = \sigma k = \sigma \left( \frac{1}{\rho_2} - \frac{1}{\rho_1} \right);$$

$$f_{\text{cap}} = f_{\text{cap}}^V + f_{\text{cap}}^\omega = \Delta P \omega + \bar{\sigma} L, \quad (1)$$

where  $k$  is the mean curvature of the meniscus;  $\rho_1$  and  $\rho_2$  are the main curvature radii;  $\bar{\sigma}$  is the projection of the surface tension vector applied to the three-phase boundary on the axis connecting the solid particles;  $f_{\text{cap}}^V$  and  $f_{\text{cap}}^\omega$  are the volumetric and surface components of the capillary force.

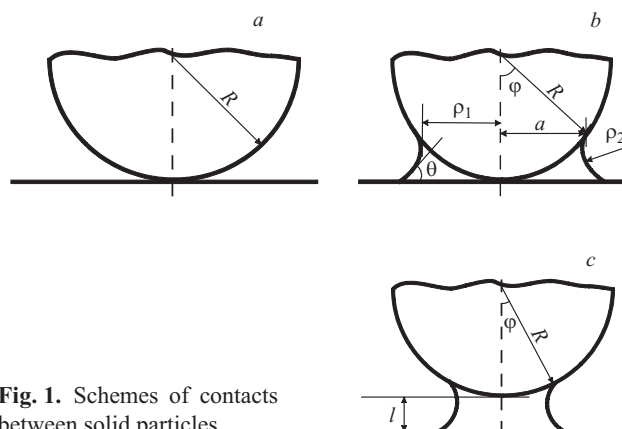
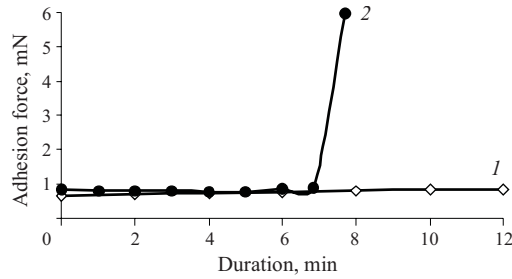


Fig. 1. Schemes of contacts between solid particles.

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**Fig. 2.** Dependence of capillary and capillary-crystallization strength on contact duration (spherical particle diameter 3.25 mm): 1) cup material  $\text{Na}_2\text{CO}_3 - \text{Na}_2\text{SO}_4$ , initial concentration 0.5 M, weight of liquid on the spherical particle at the initial moment 0.0033 g; 2) cup material — distilled water; weight of liquid on the spherical particle at the initial moment 0.0023 g.

After geometrical transforms of Eq. (1) for a contact between two balls with zero clearance ( $l = 0$ ), Fisher obtain the following formula:

$$f_{\text{cap}} = \frac{2\sigma\pi R}{1 + \tan \frac{\varphi}{2}},$$

where  $\sigma$  is the surface tension of liquid;  $\varphi$  is half of the central angle on which the liquid cup rests.

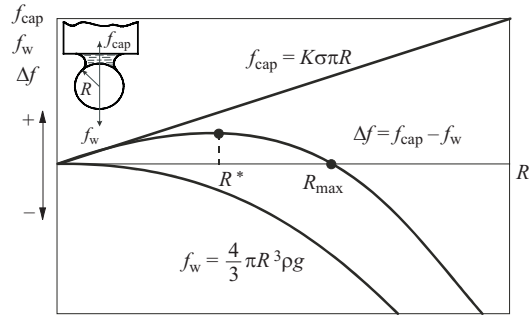
For a small volume of liquid ( $\varphi \rightarrow 0$ ) the force takes the value of  $2\sigma\pi R$  and for a completely filled capillary cell  $f_{\text{cap}} = \sigma\pi R$ .

Thermodynamic analysis of capillary interaction of particles via a liquid phase (Fig. 1b and c) has shown that the force of adhesion can be determined using the following formula from [6]:

$$f_{\text{cap}} = 2V_1 \frac{dP_1}{dl} + \sum_{ij} \sigma_{ij} \left( \frac{\partial \omega_{ij}}{\partial l} \right)_k, \quad (2)$$

whose components in the simple case correspond to the summands of formula (1); indexes  $i$  and  $j$  indicate the phases: 1) liquid, 2) solid, 3) gaseous phase. The use of formula (2) makes it possible to extend the analysis of the capillary interaction of the phases, in particular, to describe the dependence of the interaction force on the distance between the particles and the volume of liquid.

For experimental study of adhesion forces we used the model of a spherical particle – liquid interlayer – flat substrate capillary contact. This type of contact can well simulate real disperse systems. Figure 2 shows the dependences of the capillary strength of adhesion of a glass sphere to a glass plate via a cup of distilled water or  $\text{Na}_2\text{CO}_3 - \text{Na}_2\text{SO}_4$  solution. The experiments were performed on an experimental plant [7]. In the first case the cup volume decreases with time due to evaporation of liquid, while the capillary adhesion force grows. When particles interact via an interlayer of



**Fig. 3.** Dependence of forces acting upon a ball stuck from beneath to a horizontal plane on the ball radius.

the aqueous solution, the formation of a crystalline phase is registered, as a consequence of the concentration of the components in the evaporation of a liquid. The first stage of this interaction is determined by capillary force  $f_{\text{cap}} \approx 0.8\sigma\pi R$  and after the transition to the crystallization interaction the strength of particle adhesion grows by an order of magnitude.

The growth of the capillary force in the case of the solution is presumably compensated by decreased surface tension, as well as a displacement of particles by the salt film. The specifics of crystallization interaction are insufficiently studied, whereas capillary forces are analyzed in detail both for low-temperature liquids and for melts [6].

The capillary force in a disperse system usually significantly exceeds molecular, gravitational, magnetic and other kinds of interactions between solid particles. In melts the role of capillary forces becomes even more significant. Let us compare the force of adhesion of particles through a liquid cup and the force of gravity (Fig. 3) using the reduced capillary force

$$f_{\text{cap}} = K \sigma \pi R \cos \theta, \quad (3)$$

where  $K$  is a coefficient which for a particular shape of particle depends only on the amount of liquid and  $\theta$  is the wetting angle.

Thus, as the sphere adheres to the plane,  $K$  varies from 2 to 4, the maximum value corresponding to a vanishingly small volume of the cup. The use of Eq. (3) makes it possible to determine the maximum size of a particle capable of sticking to a flat surface from beneath by means of capillary force. Figure 3 shows the effect of the gravity field on the overall force of adhesion of the ball to the plane, where the weight  $f_w$  and the capillary force  $f_{\text{cap}}$  are directed oppositely.

By correlating the forces  $f_w$  and  $f_{\text{cap}}$  we obtain the formula

$$R_{\text{max}} = \sqrt{\frac{3K\sigma \cos \theta}{4\rho g}}.$$

TABLE 1

Particle diameter, mm	Ratio $f_{\text{cap}}/f_w$ in contact of a spherical particle with a plane under surface tension, mN/m		
	72.8	150	600
2.0	1.67	3.44	13.76
0.5	26.72	55.05	$2.2 \times 10^2$
0.1	$6.7 \times 10^2$	$1.4 \times 10^2$	$5.5 \times 10^3$

By equating the derivative  $d\Delta f/dR$  to zero, we find the radius of the particle corresponding to the maximum force difference  $\Delta f$ :

$$R^* = \frac{R_{\text{max}}}{\sqrt{3}}.$$

If we deal with a water cup ( $\sigma = 72.8$  mN/m) with  $\Delta\rho = 2500$  kg/m<sup>3</sup>,  $K = 3$ ,  $\theta = 0$ , then the particle diameter  $d_{\text{max}} = 5.2$  mm, whereas for salt-oxide melts ( $\sigma = 150$  mN/m)  $d_{\text{max}} = 7.4$  mm. For a cup formed by a silicate melt ( $\sigma = 600$  mJ/m<sup>2</sup>)  $d_{\text{max}} = 14.8$  mm, i.e., for systems with increased surface energy the role of capillary forces is significant even for the behavior of relatively large particles.

With decreasing particle size the ratio of the capillary force to the weight  $f_{\text{cap}}/f_w$  grows intensely. We illustrate this in Table 1 by the dependence of the  $f_{\text{cap}}/f_w$  ratio on the diameter of the spheroid particle for different surface tension values ( $\rho = 2.5$  g/cm<sup>3</sup>,  $\theta = 0$ ,  $f_{\text{cap}} = 3\sigma\pi R$ ).

With the liquid volume  $V_1 \rightarrow 0$  the surface areas  $\omega_{13}$  and  $\omega_{12}$  tend to zero, therefore,  $f_{\text{cap}}^\omega \rightarrow 0$  as well [6]. The volumetric component of the capillary adhesion  $f_{\text{cap}}^V$  is proportional to  $V_1$  ( $dk/dl$ ). If the flat cross-section of regular-shaped particles is described by a first-order curve (a cone) along the axis connecting these particles, then for such particles  $dk/dl = \text{const}$  and for  $V_1 \rightarrow 0$  the force also tends to zero. If the section is described by a second-order curve (a sphere) then for  $V_1 \rightarrow 0$  the derivative  $dk/dl \rightarrow \infty$ . After taking the limit we obtain the force of the capillary adhesion of two spherical particles for  $V_1 \rightarrow 0$  equal to  $2\sigma_{13}\pi R$  and the adhesion of a sphere to a plane equal to  $4\sigma_{13}\pi R$  [6]. For the contact between two spherical particles this deduction is validated by the analysis of formula (2). The dependence of the force on the volume is determined by the equation in [6]:

$$\frac{df_{\text{cap}}}{dV_1} \approx -\frac{\bar{\omega}_{12}}{2V_1} \Delta P.$$

In the case of menisci that are concave from the side of the liquid (with small contact angles  $\theta$ ) the derivative  $df_{\text{cap}}/dV_1$  is negative, since

$$\Delta P = P_3 - P_1 > 0.$$

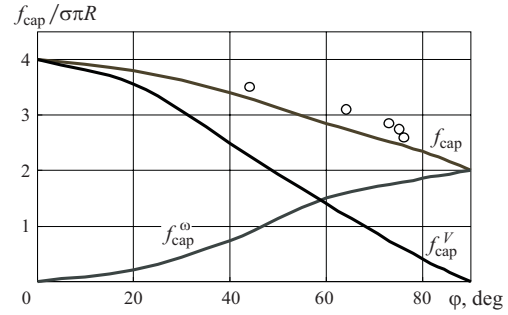


Fig. 4. Dependence of reduced capillary force and its components on the quantity of liquid in the cup in contact between a spherical and a flat particle.

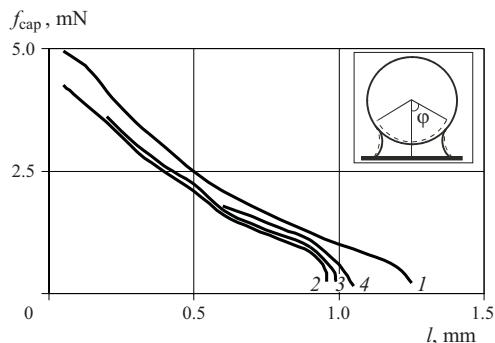
Therefore, the force of adhesion decreases as the cup volume grows. Obviously with  $\theta > 90^\circ$  the meniscus is convex from the liquid side and the derivative  $df_{\text{cap}}/dV_1$  is larger than zero. The variations in the force  $f_{\text{cap}}^V$ ,  $f_{\text{cap}}^\omega$ , and  $f_{\text{cap}} = f_{\text{cap}}^V + f_{\text{cap}}^\omega$  depending on the cup size characterized by the angle  $\phi$  (Fig. 1) under perfect wetting and zero clearance is shown in Fig. 4 [6]. The experimental dots have been obtained for a silicate melt capillary interlayer (40% SiO<sub>2</sub>, 20% Al<sub>2</sub>O<sub>3</sub>, and 40% CaO) binding chemically inert model particles (molybdenum). The wetting angle of the particle surface is close to zero (at a temperature of 1320°C).

Under low volumes of the cup the component  $f_{\text{cap}}^V$  determined by the meniscus curvature is maximum, since the curvature radius  $\rho_2$  is small. The force  $f_{\text{cap}}^\omega$  in this case, on the contrary, is close to zero. The resultant force is maximum as well. As the liquid volume increases (up to  $\phi = 90^\circ$ ), the role of the first summand ( $f_{\text{cap}}^V$ ) in Eq. (1) vanishes to zero and the role of the second summand grows. The wetting perimeter reaches the value of  $2\pi R$  and the second term, accordingly, becomes equal to  $2\sigma\pi R$ . Note that for a ball and a plane the force  $f_{\text{cap}}$  decreases from  $4\sigma\pi R$  to  $2\sigma\pi R$  for the volume variation corresponding to the angle  $\phi$  increasing from 0 to  $90^\circ$ , whereas for two balls of the same radius this force varies from  $2\sigma\pi R$  to  $\sigma\pi R$ , i.e., becomes half as much.

The force variation as a consequence of displacement of particles is controlled by the relation in [6]:

$$\frac{df_{\text{кан}}}{dl} = -\frac{\bar{\omega}_{12}^2}{2V_1} \Delta P.$$

Consequently, for concave (from the liquid side) cups the force decreases with increasing distance between the particles, the more intensely the smaller the volume of the liquid interlayer. To validate the obtained formula we give the experimental dependence of the capillary attraction force of a quartz ball ( $R = 0.13$  cm) to the surface of a plate made of an inert material (molybdenum) (Fig. 5).



**Fig. 5.** Variation in force of adhesion of a quartz ball to a flat surface via the silicate melt cup at 1320°C. The force is determined: 1) at the moment of contact of a silicate melt drop with a quartz ball; 2, 3, and 4) 38, 56, and 77 min after the start of the contact, respectively.

Due to the dissolution of quartz in the melt (initial composition: 40%  $\text{SiO}_2$ , 20%  $\text{Al}_2\text{O}_3$ , 40%  $\text{CaO}$ ); initial angle  $\varphi = 60^\circ$ ) the position of the curves  $f_{\text{cap}} = f(l)$  changes with time. In particular, the radius of the spherical surface has decreased, which has led to a decrease in the capillary force.

Figure 5 illustrates the processes in a glass batch after the formation of silica melt drops contacting with quartz sand grains.

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